THE INSECTICIDAL PROPERTIES OF SOME ESTERS OF PHOSPHORUS ACIDS

BY

GEORGE FRANKLIN LUDVIK

A.B., University of Illinois, 1941
A.M., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN ENTOMOLOGY
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R. UNIV. BIBLIOTHEEK LEIDEN

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Introduction

Following the end of hostilities in Europe in 1945, various Allied scientific investigation teams entered Germany to obtain all manner of technical information and data. As a result of these activities, numerous reports have been issued by the British and United States governments on all phases of German scientific endeavor before and during the war.

Among the insecticides reported, *Bladan,* a formulated nicotine substitute, attracted considerable attention because its active ingredient, hexaethyl tetraphosphate was a unique synthetic organic insecticide.

Ludvik and Decker (1947), considering the uniqueness of hexaethyl tetraphosphate as an economic poison, undertook a study of various phosphorus acid nuclei with differing substituent groups in an effort to circumscribe the toxicity of organic phosphorus compounds in general.

Probably the most important single account to date of research on the chemistry of phosphorus acid esters and their insecticidal properties is that of Schrader (1947), covering, among others, the three phosphorus acid esters now quite well known to American economic entomologists: hexaethyl tetraphosphate, tetraethyl pyrophosphate, and diethyl *p*-nitrophenyl phosphate.

Data available at present indicate that the effectiveness of the organic phosphate esters is due to their inhibition of cholinesterase (DuBois and Mangun, 1947; Chadwick and Hill, 1947).

Experimental Procedures

Cultures of the green peach aphid, *Myzus persicae* (Sulz.)

were maintained on potted eggplants, and cultures of the aphid *M. porosus* Sanderson, were maintained on potted rose plants. Larvae of the black carpet beetle, *Attagenus piceus* (Oliv.), were reared in a medium consisting of two per cent Brewers' yeast in chick starter mash. Five day old adults of the standard N.A.I.D.M. strain of the house fly, *Musca domestica* L., were used in contact spray and residual tests. The rearing procedure used was that described for the Peet-Grady method in Soap Blue Book (1946). *Myzus persicae, M. porosus,* and *Musca domestica* were used as test insects for determining the effects of the chemicals as contact sprays. In the case of *M. persicae,* tests were made only at a dilution of one to 500, whereas with *M. porosus,* sufficient subsequent dilutions were made to determine the range of effectiveness of the chemical under consideration. Contact spray tests against adult house flies were carried out in accordance with the small chamber method developed by Kearns and March (1943). Tests for residual activity were made by exposing five day old, adult house flies for 30 minutes to deposits on glass of 50 milligrams of chemical per square foot of surface area. Circles of wool, two square inches in area, were treated with 12.5 milligrams of chemical. Following the death of all carpet beetle larvae of the initial infestation, subsequent infestations were made to determine the duration of the residual activity. Observations of mortality in all insects except *Attagenus piceus* were made the day after treatments or exposures were completed. The results of the contact spray tests were checked for significance by analysis of variance as outlined by Snedecor (1938).

Summary

One hundred thirty-two organic esters of phosphorus acids, namely metaphosphoric, orthophosphoric, pyrophosphoric, triphosphoric, and phosphorous acids, were examined for possible activity as contact insecticides against the green peach aphid, *Myzus persicae* and the house fly, *Musca domestica.* Twenty-six compounds were found to possess at

least a fair degree of insecticidal activity, and were tested further as contact sprays against a more resistant aphid, *Myzus porosus,* and against the house fly. Twenty-four of these compounds exhibited fair to extreme toxicity to *M. porosus,* while only 19 showed varying degrees of toxicity to the house fly. Of the 26, only three compounds proved to be active residual toxicants to the house fly. Seven compounds were shown to give good to fair protection of wool from the feeding of the larvae of the black carpet beetle, *Attagenus piceus.*

Comparisons of chemical structures in relation to toxicity indicated that certain essential chemical components were necessary to impart high toxicity in organic phosphate esters. The first requirement was that the phosphorus atom must be pentavalent, and that two of the valances must be linked with those of an oxygen atom. The second requirement was that two of the remaining valances must be occupied by OR groups. The limits of R were established as being ethyl or isopropyl. The third and final requirement was that an OR′ group must occupy the remaining valence. It was shown that R′ may be a relatively large alkyl group, acyl group, aryl group or an arylacyl group. The generalized structure necessary for high toxicity in an organic phosphate ester was therefore established as $(RO)_2P(O)OR'$, with definite limits determined for R and R′. This essential structure accounted for the toxicity of all compounds studied except in the case of ethyl metaphosphate. The replacement of $P=O$ by $P=S$ resulted in decreased toxicity of toxic compounds. The toxicity of certain phosphoric esters was shown to increase as the length of the normal alkyl chain was increased to an optimum of about eight carbon atoms. Iso-derivatives were shown to be of the same order of activity as their next lower normal homologues.

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VITA

George Franklin Ludvik was born August 12, 1919 in Dearborn, Michigan, the son of Benjamin Edward and Olga Thal Ludvik. He completed his grammar school education at Dearborn Junior High School in June, 1933 and his high school education at Dearborn High School in June, 1937. In September, 1937 he enrolled at the University of Illinois. In June, 1941 he graduated from the University of Illinois, receiving a Bachelor of Arts degree in Entomology. He continued his education at the University of Illinois in September, 1941 and was appointed a Special Research Assistant with the Illinois Agricultural Experiment Station and the Illinois Natural History Survey. In October, 1942 his education was interrupted when he was inducted into the Army of the United States. He served mainly with medical units and was honorably discharged in January, 1946 with the rating of Technician Fourth Grade. He re-entered the University of Illinois in February, 1946 and was appointed Special Research Assistant with the Illinois Agricultural Experiment Station and the Illinois Natural History Survey. He received a Master of Arts degree in Entomology in February, 1947 and continued his graduate studies in Entomology at the University of Illinois.

He was married to Virginia Ellen Walsh in Albion, Illinois, June 13, 1942. Their daughter, Nancy Ellen, was born August 16, 1947 in Urbana, Illinois.

He is a member of Phi Sigma, Gamma Sigma Delta, and an associate member of Sigma Xi. He belongs to the American Association of Economic Entomologists and the Illinois Academy of Science.

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